

## MOLECULE FORMATION. I. IN NORMAL H I CLOUDS

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## ABSTRACT

We study the formation of simple molecules employing both gas-phase reactions and catalytic surface reactions on interstellar grains. We show that it is likely that interstellar grains will grow mantles, and we follow the variation in molecular abundances and mantle composition as the cooling elements deplete onto the grains, causing a cloud to heat up and expand. It is found that CH, CH<sup>+</sup>, CO, and CN are most abundant when the clouds are dense ( $n_H > 50 \text{ cm}^{-3}$ ) and cold ( $T < 50^\circ \text{ K}$ ), while OH and NH are most abundant when  $n_H \approx 30 \text{ cm}^{-3}$  and  $T \sim 50^\circ \text{ K}$ . The grain grows to a maximum size of about  $0.16 \mu$  in about  $10^8$  years, and the mantle is composed primarily of CH<sub>4</sub> in the inner parts and of H<sub>2</sub>O in the outer parts.

*Subject headings:* abundances, interstellar matter — molecules, interstellar — interstellar grains

## I. INTRODUCTION

Increasing numbers of interstellar molecules have been discovered during recent years, the total number of molecules as of 1971 September being about 20. The list ranges from the simplest diatomics, H<sub>2</sub>, CH, CH<sup>+</sup>, CN, OH, and CO, through intermediate molecules like H<sub>2</sub>O, NH<sub>3</sub>, and H<sub>2</sub>CO, to complex molecules like CH<sub>3</sub>C<sub>2</sub>H and HCOCH<sub>3</sub>. The simplest molecules are in general widely distributed in interstellar space and occur in the typical interstellar clouds. The more complex molecules seem to be less widely distributed and are found in or in association with special types of objects, e.g. H II regions, infrared sources, and dense dust clouds. In the latter sources one also observes a wide range of anomalous excitation effects (masing). However, because certain radiation fields in interstellar space (ultraviolet, X-ray, cosmic ray) are capable of destroying molecules, even the mere existence of simple molecules indicates that formation mechanisms are quite effective. In this work we consider primarily the formation of simple molecules and their role in the chemistry and physics of the interstellar medium.

Bates and Spitzer (1951) attempted to explain the abundance of CH and CH<sup>+</sup> through radiative association, but found values that were smaller than those observed by three orders of magnitude. These authors proposed that sublimation of CH<sub>4</sub> in the grains could be an important source for circumstellar CH<sup>+</sup>. However, the same mechanism may not work equally well in typical interstellar clouds since it relies upon a nearby star to raise the grain temperature to  $20^\circ \text{ K}$ . Breakup of dirty ice grains by low-energy cosmic rays as a source of interstellar molecules has been studied by Hayakawa (1960), Kimura (1962), and Takayanagi (1964). This process is efficient only for very small grains. Breakup of polyatomic molecules ejected from cool, luminous stars has been proposed by Tsuji (1964), and a similar process operating in preplanetary systems has been proposed by Herbig (1970). However, in view of the short lifetime of molecules in fairly unshielded regions, it is questionable whether the molecules will survive long enough to become widely distributed in the interstellar medium. The wide distribution of CH, CH<sup>+</sup>, CN, OH, CO, and H<sub>2</sub>CO in "normal" clouds seems to imply that at least these molecules are formed in situ.

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Solomon and Klemperer (1971; Klemperer 1971) have recently proposed gas-phase reactions in ordinary, cold clouds that are able to produce CH, CH<sup>+</sup>, CN, and CO in reasonable agreement with observations. However, the abundance of OH cannot be explained by gas-phase reactions in cold clouds, except where the densities become very large ( $n_H \gtrsim 10^4 \text{ cm}^{-3}$  [Julienne, Krauss, and Donn 1971]). Since H<sub>2</sub> is observed (Carruthers 1970) and the only known efficient formation mechanism is recombination on grain surfaces with subsequent ejection into the gas phase (Hollenbach, Werner, and Salpeter 1971), it is suggestive that the same mechanism may be responsible for forming the OH molecules. Here we investigate the formation of simple molecules by both cold gas-phase reactions and surface reactions on interstellar grains.

The composition and size of the interstellar grains are important in determining the molecular abundances from the processes above. Assuming that surface reactions do not lead to ejection, van de Hulst (1949) showed that the grains could accumulate a mantle of  $10^{-5} \text{ cm}$  in  $\lesssim 10^8$  years, with a majority of the mass being C, N, and O atoms, this mantle being composed of "dirty ice." This process implies that the gas will gradually become depleted in heavier atoms, which, because C and O are effective coolants in the gas phase, offers a possibility of explaining the observed high cloud temperatures (Field, Goldsmith, and Habing 1969). Observationally, interstellar Na, Ca, Ti, and K are usually less abundant than in the stars if low-energy cosmic rays are present (Habing and Pottasch 1967; Howard, Wentzel, and McGee 1963; Habing 1969). In this work we also follow in detail the evolution of normal interstellar clouds as cooling elements deplete onto the grains and the grains grow mantles. As part of the reacting species leave the grain as molecules, we find that such clouds contain a significant number of simple molecules. In a subsequent paper (hereinafter referred to as Paper II) we treat in detail both hot gas-phase reactions and the destruction of grains in interstellar shock waves as a source for simple molecules in interstellar space.

In § II we discuss the requirements for recombination reactions to occur on interstellar grains with the subsequent buildup of a molecular mantle. Together with § III, in which we discuss depletion and heating of the evolving gas, this forms the basis for a treatment of the precollision history of dust and gas which also serves as the initial conditions in Paper II. In § IV we give all the chemical reactions included in the calculations. In § V we give the results of calculations for two values of the intercloud pressure and for a range of cloud masses. The discussion is in § VI.

## II. GRAIN GROWTH

We assume that the grain starts out as a spherical core of graphite or silicates of radius  $0.05 \mu$  and that the grain temperature is in the range  $10^\circ\text{--}15^\circ \text{ K}$  (Greenberg 1971). In order for efficient mantle growth through molecule formation to occur, it is necessary that (a) the residence times of atoms be long enough for recombination to occur, (b) the recombination can occur through interaction with the lattice, (c) the formation energy be dissipated through the lattice so that the molecule is not immediately removed from the grain, and (d) the newly formed molecule have a residence time that is long compared with the formation of a monolayer. Since an acquired mantle changes the surface properties of the core, these requirements should be investigated for the mantle surface as well as for the core.

The nature of the adsorption forces on interstellar grains is largely unknown. For a graphite grain, physical adsorption is the most likely process, while electrostatic forces may be the most important for silicate grains. Using the expressions for physical adsorption on graphite as given by Hellemans, van Itterbeek, and van Dael (1967) and the ratios of van der Waals coefficients, we have calculated binding energies for the most abundant atomic species. The corresponding maximum grain temperatures for recombination with H atoms (Knaap *et al.* 1967) as determined from requirement (a)

above are listed in column (2) of table 1. Employing expressions as given by Augason (1970), we have listed the results for a silicate core in column (3) of table 1.

For grain temperatures  $\geq 10^\circ \text{K}$ , formation of hydrogen molecules may not be very efficient, and the formation of a hydrogen mantle will require unusually low grain temperatures (Greenberg and de Jong 1969). According to the picture developed by Hollenbach and Salpeter (1971),  $\text{H}_2$  will probably form only on the impurity sites of the core. The growth of the grain is therefore not influenced by this process, and we may limit our attention to the heavier molecules.

We see that if the graphite grain has a temperature less than  $16^\circ \text{K}$  and the silicate grain less than  $13^\circ \text{K}$ , recombination of the heavier atoms can take place on the surface of the core. (It is assumed that  $\text{C}^+$  is neutralized upon colliding with the negatively charged grain and that the electronic recombination process does not affect the sticking rate of  $\text{C}^+$ . However, as recently pointed out by Watson and Salpeter [1972*a*], the sticking rate could be substantially reduced.) Assigning a probability of  $1 - \alpha$  that a formed molecule may be ejected from the grain upon formation, we will assume that  $\text{OH}$ ,  $\text{CH}$ , and  $\text{NH}$  form on the grain and that these molecules stay on the surface with a probability  $\alpha \approx 0.5$ . Furthermore, since the adsorption energy of these diatomic radicals will quite likely be larger than the corresponding atomic adsorption energies, we may assume that subsequent recombinations will also take place, leading to the stable molecules  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ . We have here assumed that  $\text{H}_2\text{O}$  and  $\text{NH}_3$  may form in an interaction with lattice electrons (Williams 1968) while  $\text{CH}_4$  may form in an interaction with lattice phonons. The stable molecules all have a residence time that is longer than the time for formation of a monolayer as long as the grain temperature is below about  $50^\circ \text{K}$ . Therefore, since the estimated grain temperatures are lower than  $50^\circ \text{K}$ , we find that a mantle of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$  will begin to form as mentioned above in item (*d*).

In the first few monolayers (which form on a timescale of  $\sim 10^4$  years) the relative abundance of  $\text{CH}_4$  is 54 percent, of  $\text{H}_2\text{O}$  29 percent, and of  $\text{NH}_3$  4 percent by number. No adsorption energies are known for a surface of this composition. We choose to calculate adsorption energies due to a pure  $\text{CH}_4$  solid and a pure  $\text{H}_2\text{O}$  solid and use the combination rule  $q_{\text{comb}} = (q_{\text{methane}}q_{\text{ice}})^{1/2}$  for an estimate of the composite properties. The effects of  $\text{NH}_3$  as well as other components are neglected. These calculations are based on the general expression for physical adsorption given by Steel and Ross (1961) and ratios of the van der Waals coefficients for the heavier atoms. Because of uncertainty as to the crystal structure of the mantle material, we have assumed that the solids have a simple cubic structure. The maximum temperatures for the recombination with H atoms on the mantle are given in columns (4)–(6) of table 1.

We find that, in order for a mantle to continue to form out of all the heavier atoms, the grain temperature must be below about  $15^\circ \text{K}$ . Although grain temperatures less than about  $15^\circ \text{K}$  are what is expected in the general interstellar medium, one should

TABLE 1  
MAXIMUM GRAIN TEMPERATURES FOR RECOMBINATION WITH H ATOMS

Recombining Atom (1)	$(T_{\text{gr}})_{\text{max}}$ (Graphite) [ $^\circ \text{K}$ ] (2)	$(T_{\text{gr}})_{\text{max}}$ (Silicate) [ $^\circ \text{K}$ ] (3)	$(T_{\text{gr}})_{\text{max}}$ (Methane) [ $^\circ \text{K}$ ] (4)	$(T_{\text{gr}})_{\text{max}}$ (Ice) [ $^\circ \text{K}$ ] (5)	$(T_{\text{gr}})_{\text{max}}$ (Methane-Ice) [ $^\circ \text{K}$ ] (6)
H.....	9	11	5	13	8
O.....	16	13	16	30	22
$\text{C}^+$ .....	37	35	33	63	46
N.....	23	19	22	42	31

note how sensitive the chemical makeup of the grain is to variations in its temperature. For temperatures larger than about 20° K, it is unlikely that recombination with H atoms would take place on the general surface. However, recombination among only the heavier atoms could then occur, and heavy molecules would be formed both in the mantle and in the gas phase.

Some of the more abundant, nonreactive atoms may get “trapped” in the surface layers. For He and Ne we find, however, that their residence times are much less than the time it takes to form a monolayer. But the other heavy atoms will all be part of the mantle as the grain grows.

Observational evidence (Knacke, Cudaback, and Gaustad 1969; Gillett and Forrest 1973) shows that in the general interstellar medium the amount of ice in interstellar grains is less than or about 10 percent by mass. If this were to be satisfied by the mantle formation as outlined above, it would mean that the grains on the average never grow beyond a radius  $\sim 0.06 \mu$  before the mantle is destroyed. Although the minimum detectable concentration of water may be somewhat greater when the effect of methane, ammonia, and silicates on the ice absorption band is taken into account (Hunter and Donn 1971), larger mantles would be limited to clouds either more dense than average or “older” than average (having escaped cloud collisions which could cause removal of the mantle). Another possible explanation of the observed limit on water in the grains is that the mantle material will rapidly be modified in composition through interactions with either ultraviolet radiation (Donn and Jackson 1970) or cosmic-ray radiation (Shulman 1970). Such processes have been neglected in this work.

### III. DEPLETION AND HEATING

The main cooling agents in an interstellar cloud under ordinary conditions are the trace elements O, C<sup>+</sup>, Fe<sup>+</sup>, and Si<sup>+</sup>. In their model for interstellar gas based on cosmic-ray heating (hereafter referred to as the FGH model) Field *et al.* (1969) were forced to assume that these elements were depleted from the gas. The state of depletion depends on the sticking probability of the atoms on the grain surface. Sticking probabilities  $s(T)$  have been calculated using the expression given by Hollenbach and Salpeter (1970). In the range of temperatures in this phase, sticking probabilities for all the heavier atoms are essentially unity, except for Ne. Ne and the light atoms H and He do not stay on the grain even if they thermalize, since their residence times on the grain surface are much shorter than the formation time for a monolayer when the grain has a temperature  $\geq 12^\circ$  K.

Thus, all elements except H, He, and Ne can become part of the mantle as the grain grows. The depletion of element  $i$  is governed by

$$\frac{dn_i}{dt} = -n_i u_i \pi a^2 n_g \alpha_i, \quad (1)$$

which allows us to write (Mészáros 1972) for the depletion factor

$$d_i \equiv \frac{n_i}{n_{i0}} = \left( \frac{n_1}{n_{10}} \right)^{u_i \alpha_i / u_1 \alpha_1}. \quad (2)$$

Here  $n_{i0}$  is the abundance at time  $t = 0$  and  $n_1$  denotes the abundance of a reference element which we take to be oxygen. The quantity  $n_g$  is the number density of grains,  $a$  is the grain radius,  $\alpha_i$  is the probability that species  $i$  will become permanently locked up in the grain,  $\alpha_i = \alpha_{si}(T)$ , and

$$u_i = \left( \frac{8 kT}{\pi m_i} \right)^{1/2} (1 + yZ_i), \quad (3)$$



where  $Z_i$  is the charge of species  $i$  with mass  $m_i$  and  $y$  is found from the equation describing the balance of charge on the grain. This formula takes account of the greater effective cross-section for charged species.

The grain charge will be determined mainly by the electrons and protons produced in cosmic-ray ionization of hydrogen. The contribution to the electron density from photoionization of trace elements is largest when the temperature is low,  $T \sim 20^\circ \text{ K}$ , and before any significant depletion has occurred, and is about 20 percent of the contribution by cosmic-ray-produced electrons. This gives the value  $y = 2.82$ . However, as depletion occurs and the gas heats up,  $y$  decreases rapidly to its asymptotic value of 2.5, due to cosmic-ray ionization alone. In equation (3) we have neglected any variation in  $y$  and have used the value of 2.5. It is clear from equation (3) and equation (2) that charged species will be preferentially depleted relative to neutral species by fairly large factors.

Mészáros (1972) has investigated the time-dependent evolution of interstellar gas as the depletion of cooling agents causes the gas to heat up and expand under a constant external pressure, neglecting gravitational effects. Here we have used essentially the same treatment. One may compensate somewhat for the neglect of gravitation by using a higher external pressure which also tends to keep a cloud "in." Mészáros's work offers a detailed explanation of the procedures used. In our work we have included variable sticking factors and have added molecular formation rates (§ IV). Also, some of the cooling rates have been revised (Paper II, § IV).

Since we have neglected gravitational effects during the expansion, the treatment here is strictly valid only in the limit of a zero-mass cloud. However, for clouds that are far from being gravitationally unstable, such a case is still representative. The exact numerical criterion for instability is uncertain, since turbulence, rotation, and magnetic fields could play an important role. We have treated clouds with masses of 50, 200, 500, and 1000  $M_\odot$  over a temperature range  $T = 20^\circ\text{--}100^\circ \text{ K}$ . Since the maximum stable mass  $M_{\text{max}} \propto T^2$  (Spitzer 1968), the zero-mass treatment may represent the larger clouds only for the higher temperatures.

One cooling mechanism that would not be affected by the depletion would be the cooling due to the grains themselves. However, for temperatures less than about  $100^\circ \text{ K}$ , this contribution is small relative to the cooling by oxygen atoms as long as oxygen is not depleted by more than a factor of 10. Since we will find that in our case the O abundance in general is not depleted by more than a factor of 3, we have neglected grain cooling.

#### IV. CHEMICAL REACTIONS

Table 2 lists all the two-body gas-phase reactions that we have included. The rate of formation of CH, OH, or NH on the surface of the grains is  $k_g = s(1 - \alpha)\pi a^2 \times (1 + 2.5Z)n_gnv$ , where  $a$  is the grain radius,  $n$  denotes the abundance of  $\text{C}^+$ , O, or N,  $Z$  is the charge of the atom,  $s$  is its sticking coefficient, and  $v$  is the mean speed. Thus, the rate constant for this process is  $k_g/(n_H n) \approx 6 \times 10^{-9}(1 + 2.5Z)a^2 T^{1/2}$  ( $\text{cm}^3 \text{ s}^{-1}$ ).

The photodestruction rates are clearly very important in these relatively low-density clouds. For the interstellar radiation field with  $\lambda > 912 \text{ \AA}$ , we use the results of Habing (1968), who obtained an energy density  $U_\lambda \sim 4 \times 10^{-17} \text{ erg cm}^{-3} \text{ \AA}^{-1}$  at  $\lambda \sim 1000 \text{ \AA}$ . For the nonattenuated destruction rates of CO, CN,  $\text{CH}^+$ , and CH we have adopted the values given by Solomon and Klemperer (1971). For OH we calculate a photodissociation rate for the transitions  $^2\pi \rightarrow ^2\Sigma^-$  and  $^2\pi \rightarrow ^2\Sigma^+$  assuming that the  $f$ -value for each transition is  $\sim 10^{-3}$  (Solomon 1968). This value of  $4 \times 10^{-12} \text{ s}^{-1}$  is close to the value given by Stecher and Williams (1966) based on a Bates-Spitzer radiation field, but is unfortunately quite uncertain due to lack of any experimental data. We note that, since we have neglected any photodissociation to the

TABLE 2  
TWO-BODY REACTIONS IN THE PRESHOCK PHASE\*

Reaction	Rate Constant [ $\text{cm}^3 \text{s}^{-1}$ ]
$\text{C}^+ + \text{H} \rightarrow \text{CH}^+ + h\nu$ .....	$7 \times 10^{-17}$ (for $T \leq 50^\circ \text{K}$ ) $10^{-17}[7 - 0.07(T - 50)]$ (for $50^\circ \text{K} \leq T \leq 100^\circ \text{K}$ ) $\dagger$ $10^{-17}[3.5 - 0.015(T - 100)]$ (for $100^\circ \text{K} \leq T \leq 200^\circ \text{K}$ ) $\dagger$
$\text{C} + \text{H} \rightarrow \text{CH} + h\nu$ .....	$10^{-17}[3 - 0.06(T - 20)]$ (for $10^\circ \text{K} \leq T \leq 30^\circ \text{K}$ ) $10^{-17}[2.4 - 0.03(T - 30)]$ (for $30^\circ \text{K} \leq T \leq 100^\circ \text{K}$ ) $\dagger$ $3 \times 10^{-18}$ (for $T \gtrsim 100^\circ \text{K}$ )
$\text{CH}^+ + e \rightarrow \text{CH} + h\nu$ .....	$5.7 \times 10^{-9} T^{-0.7}$
$\text{CH}^+ + e \rightarrow \text{C} + \text{H}$ .....	$5.7 \times 10^{-9} T^{-0.7}$
$\text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2$ .....	$7.5 \times 10^{-15} T^{5/4}$
$\text{CH}^+ + \text{O} \rightarrow \text{CO} + \text{H}^+$ .....	$10^{-9}$
$\text{CH}^+ + \text{O} \rightarrow \text{CO}^+ + \text{H}$ .....	$10^{-9}$
$\text{CH}^+ + \text{N} \rightarrow \text{CN} + \text{H}^+$ .....	$10^{-9}$
$\text{CO}^+ + \text{H} \rightarrow \text{CO} + \text{H}^+$ .....	$10^{-9}$
$\text{CH} + \text{C}^+ \rightarrow \text{C}_2^+ + \text{H}$ .....	$10^{-9}$
$\text{C}_2^+ + \text{N} \rightarrow \text{CN} + \text{C}^+$ .....	$10^{-9}$
$\text{CH} + \text{H} \rightarrow \text{C} + \text{H}_2$ .....	$10^{-14}$
$\text{CH} + \text{O} \rightarrow \text{CO} + \text{H}$ .....	$4 \times 10^{-11}$
$\text{CH} + \text{N} \rightarrow \text{CN} + \text{H}$ .....	$4 \times 10^{-11}$
$\text{CN} + \text{O} \rightarrow \text{CO} + \text{N}$ .....	$10^{-10} e^{-1200/T}$
$\text{CN} + \text{N} \rightarrow \text{C} + \text{N}_2$ .....	$10^{-13}$
$\text{C}^+ + e \rightarrow \text{C} + h\nu$ .....	$10^{-11} T^{-1/2} [12.6 - 2.38 \log T] \ddagger$
$\text{OH} + \text{C}^+ \rightarrow \text{CO} + \text{H}^+$ .....	$10^{-9}$
$\text{NH} + \text{C}^+ \rightarrow \text{CN} + \text{H}^+$ .....	$10^{-9}$

\* From Klemperer (1971), except where noted.

$\dagger$  A straight line fitted to values given by Klemperer (1971).

$\ddagger$  From Seaton (1955).

continuum, this rate may be underestimated. The ionization threshold of OH is 13.2 eV (Allen 1963, p. 47), which is close to the Lyman limit. Assuming a cross-section  $10^{-18} \text{cm}^2$ , we estimate a photoionization rate of  $\sim 10^{-12} \text{s}^{-1}$ . Because of a lack of detailed information on the photodestruction rates of NH, we assume its dissociation rate relative to that of OH to be  $\frac{7}{3}$ , as estimated by Stecher and Williams (1966). We take the photoionization rate to be  $\sim 10^{-12} \text{s}^{-1}$ . All the nonattenuated photodestruction rates are given in table 3.

The attenuation of the radiation field is given by (Habing 1968)

$$G[a_\lambda, A(\lambda)] = [a_\lambda + (1 - a_\lambda)10^{0.4A(\lambda)}]^{-1}, \quad (4)$$

where  $a_\lambda$  is the grain albedo and  $A(\lambda)$  is the extinction (mag) at a wavelength  $\lambda$ . The extinction to the center of a cloud of mass  $M$  ( $M_\odot$ ) and average density  $n$  is

$$A(\lambda) = 2.3 \times 10^7 Q(\lambda) a^2 n^{2/3} M^{1/3}, \quad (5)$$

where  $a$  is the grain radius and  $Q(\lambda)$  is the extinction efficiency. We have assumed a dust-to-gas ratio  $n_g/n = 10^{-12}$  which corresponds to an average extinction of 1.5 mag kpc $^{-1}$  and an assumed average grain radius of 0.12  $\mu$ . The attenuation factor  $G$  changes as the grains grow and the cloud expands. The changing radius and chemical composition will also cause variations in  $G$  through  $Q_\lambda$  and  $a_\lambda$ . The latter variations are small, however, relative to the variations in  $a$  and  $n$ , and for wavelengths in the region  $\sim 1000 \text{\AA}$  we have adopted the values 0.5 and 2.5 for the albedo and the extinction efficiency, respectively. In one calculation we adopted the larger value  $Q$  ( $\sim 1000 \text{\AA}$ ) = 4.0.

TABLE 3  
NONATTENUATED PHOTODESTRUCTION RATES

Reaction	Rate [ $s^{-1}$ ]
$OH + \gamma \rightarrow O + H$ .....	$4 \times 10^{-12}^*$
$OH + \gamma \rightarrow OH^+$ .....	$\sim 1 \times 10^{-12}$
$CH + \gamma \rightarrow C + H$ .....	$5 \times 10^{-11}^\dagger$
$CH + \gamma \rightarrow CH^+$ .....	$5 \times 10^{-11}^\dagger$
$CH^+ + \gamma \rightarrow C^+ + H$ .....	$3 \times 10^{-12}^\dagger$
$CO + \gamma \rightarrow C + O$ .....	$2 \times 10^{-11}^\dagger^\S$
$CN + \gamma \rightarrow C + N$ .....	$4 \times 10^{-11}^\dagger$
$NH + \gamma \rightarrow N + H$ .....	$1 \times 10^{-11}$
$NH + \gamma \rightarrow NH^+$ .....	$\sim 1 \times 10^{-12}$
$C_2^+ + \gamma \rightarrow C^+ + C$ .....	$8 \times 10^{-12}^\dagger$
$C + \gamma \rightarrow C^+$ .....	$1.4 \times 10^{-10}^\parallel$

\* Based on work by Solomon (1968).

† From Klemperer (1971).

‡ Based on an autoionization oscillator strength of  $5 \times 10^{-2}$  at 1130 Å and a photoionization continuum cross-section of  $1.1 \times 10^{-18} \text{ cm}^2$  (Solomon and Klemperer 1971).

§ This value corresponds to a quantum yield of 0.07. According to Stief *et al.* (1972), the exact quantum yield of CO is unknown, but it could be considerably less than unity.

|| From Werner (1970).

## V. APPLICATION AND RESULTS

“Young” clouds are assumed to have normal gas-phase abundances. We have taken the number density of He to be 9 percent relative to H and taken the abundances of the trace elements from Allen (1963), except for  $Fe^+$ , where we have used the revised value of  $3.2 \times 10^{-5}$  relative to H by number (Nussbaumer and Swings 1970). The value for the intercloud pressure has been taken equal to  $1800 \text{ cm}^{-3} \text{ }^\circ\text{K}$  (which is the critical pressure as given by Field *et al.* 1969) and  $1000 \text{ cm}^{-3} \text{ }^\circ\text{K}$ . The former corresponds well to recent observations by Rhadhakrishnan *et al.* (1972), but is larger by a factor of 2 to 3 than what corresponds to observations of very cold clouds ( $T \lesssim 25^\circ\text{K}$ ) (Verschuur and Knapp 1971). However, a larger external pressure may to some extent compensate for the lack of gravitational forces in our model. We have assumed a cosmic-ray ionization rate of atomic hydrogen  $\zeta = 4 \times 10^{-16} \text{ s}^{-1}$  (Field *et al.* 1969).

Sticking probabilities for the various atoms on the mantle were calculated using the adsorption energies of the composite model except for the starting condition, where the energies for graphite were used. (The differences between the adsorption energies of graphite and silicate were neglected.) The adsorption energies for “pure” ice were used only when the total amount of  $H_2O$  was more than 50 percent of the mantle material. The resulting depletion factors are shown in figure 1. We see that the most depleted element is  $C^+$ , whose abundance is down by a factor of 30 in about  $10^8$  years. In the same time, oxygen depletes only by a factor of 2.

Figure 2 shows how the temperature and density vary as a function of the depletion of  $C^+$ . For a pressure of  $1800 \text{ cm}^{-3} \text{ }^\circ\text{K}$ , the gas heats up from the initial temperature of  $20^\circ\text{K}$  to  $\sim 100^\circ\text{K}$  as  $C^+$  depletes by a factor of  $\sim 30$ , i.e., the timescale is about  $1 \times 10^8$  years. For a pressure of  $1000 \text{ cm}^{-3} \text{ }^\circ\text{K}$ , the corresponding time is about  $1.16 \times 10^8$  years. This timescale will vary inversely with the assumed value for the

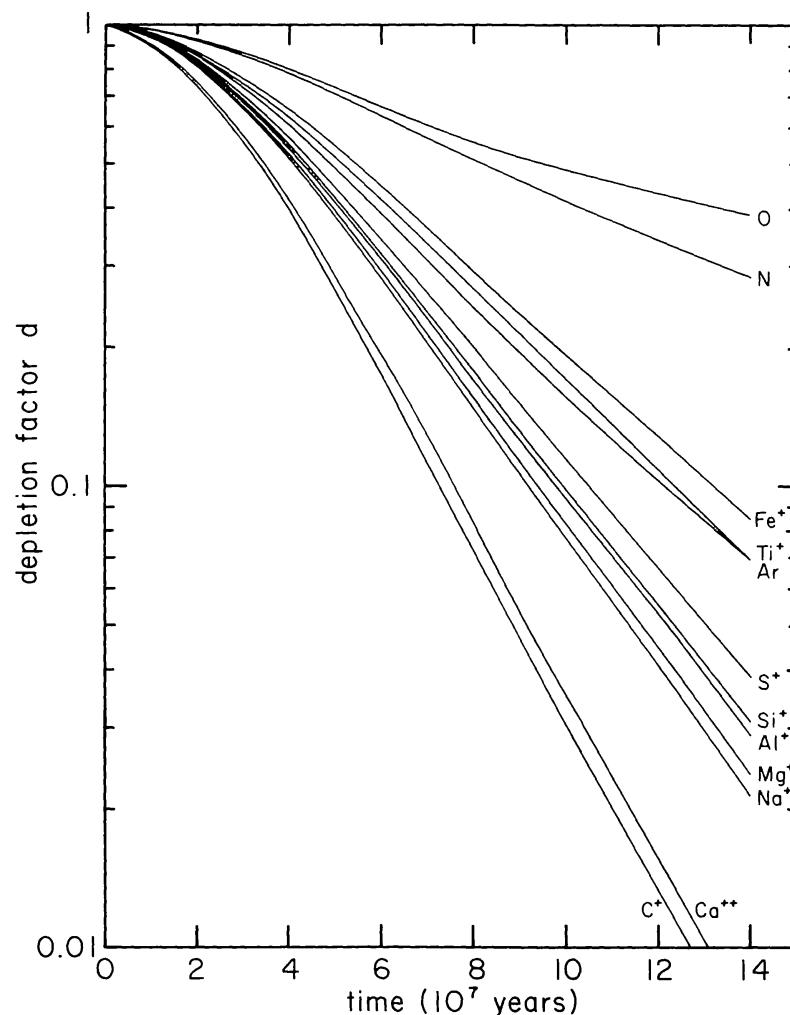


FIG. 1.—Depletion factors for the most abundant elements as functions of time. Intercloud pressure is  $1800 \text{ cm}^{-3} \text{ }^{\circ} \text{K}$ . All atoms are assumed to have the same probability ( $\alpha = 0.5$ ) of being retained in the grain as part of a molecule.

parameter  $\alpha$ , which is here 0.5. For a reasonable range in  $\alpha$ , the process of heating and expansion of clouds may therefore take place with a timescale from  $5 \times 10^7$  years to a few  $10^8$  years. It has been shown from hydrodynamic calculations (Mészáros 1973) that as the cooling elements become very depleted [ $1/d(\text{C}^+) \gtrsim 200$ ], the cloud tends to “explode” with a rapid increase in temperature and decrease in density. In this way a cloud may revert back to the stable intercloud phase from which it condensed. Although the hydrostatic treatment used here breaks down when depletion becomes very large (when the thermal timescale becomes less than the dynamic timescale), the curves shown in figure 2 differ only by about 30 percent from the correct hydrodynamic values.

Since a large part of the mantle of the grain is composed of  $\text{CH}_4$  (fig. 3), which is inert and does not bind strongly to other parts of the grain, the energy needed to remove  $\text{CH}_4$  in the postshock phase will be much less than for most other species. In order to approximately treat such a nonhomogeneous situation in the postshock phase, we have divided up the grain into two “component” grains. The mantle of one grain is composed solely of  $\text{CH}_4$  (the “ $\text{CH}_4$  grain”), while the mantle of the other



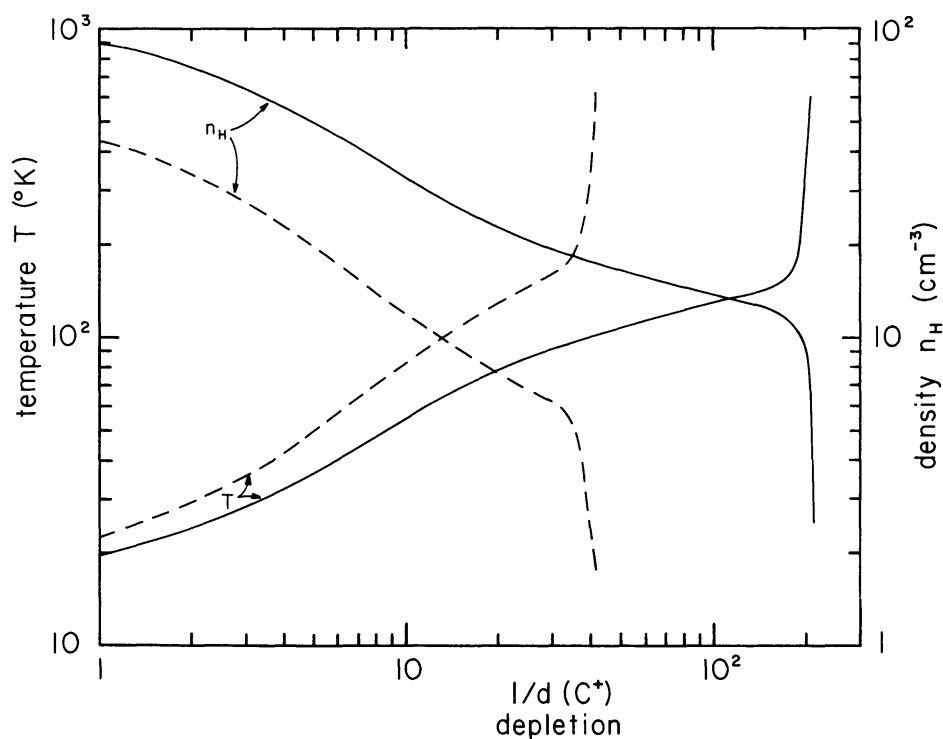


FIG. 2.—Temperature and density as functions of the depletion of  $C^+$ . *Solid curves*, external pressure of  $1800 \text{ cm}^{-3} \text{ }^\circ\text{K}$ ; *dashed curves*, pressure of  $1000 \text{ cm}^{-3} \text{ }^\circ\text{K}$ . In both cases, the probability of a gas atom being retained in the grain as part of a molecule is  $\alpha = 0.5$ . The cosmic-ray ionization rate is assumed to be  $4 \times 10^{-16} \text{ s}^{-1}$ .

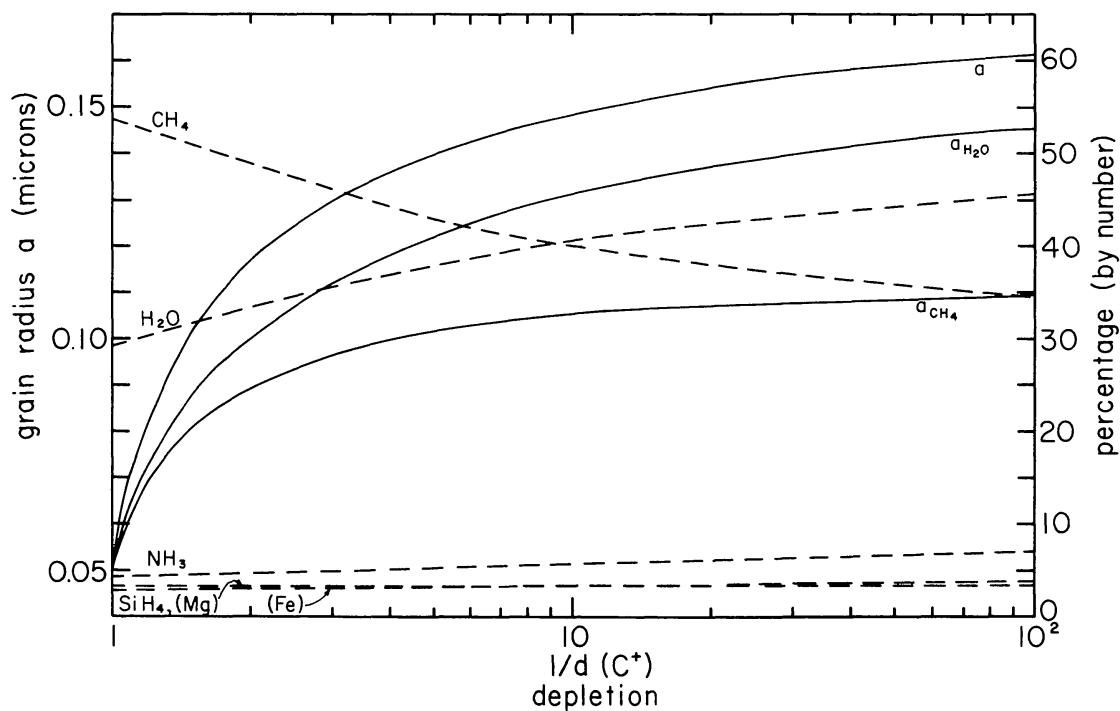


FIG. 3.—*Solid curves*, grain radii plotted versus the depletion of  $C^+$ . The  $a$  is the total grain radius;  $a_{H_2O}$  and  $a_{CH_4}$  are the radii of the two components of  $a$ , the “ $H_2O$  grain” and the “ $CH_4$  grain,” respectively. *Dashed curves*, percentage (by number) of the most abundant constituents of the mantle. Since no assumption has been made as to the possible type of molecules containing Fe and Mg, only their atomic designations are used.

grain involves all the other species (the “H<sub>2</sub>O grain”). We may express the two radii as follows:

$$a_{\text{CH}_4}^3 = \frac{3}{4\pi\rho} N_{\text{C}^+} m_{\text{C}^+} + a_0^3, \quad (6)$$

$$a_{\text{H}_2\text{O}}^3 = \frac{3}{4\pi\rho} \sum_{i \neq \text{C}^+} N_i m_i + a_0^3. \quad (7)$$

Here  $N_i = (n_i/n_g)(1 - d_i)$  and  $m_i$  is the mass of the particle with which atom  $i$  is associated in the grain. (For O, C<sup>+</sup>, N, and Si<sup>+</sup> we have used the masses of H<sub>2</sub>O, CH<sub>4</sub>, NH<sub>3</sub>, and SiH<sub>4</sub>, respectively; for any other atom we have used the atomic masses.) The initial radius of the grain is  $a_0$  and its density is  $\rho$ , assumed to be 1.5 g cm<sup>-3</sup>. The actual grain radius is given by

$$\begin{aligned} a^3 &= a_{\text{H}_2\text{O}}^3 + a_{\text{CH}_4}^3 - a_0^3 \\ &= a_0^3 \left[ 1 + \frac{3}{4\pi\rho n_g a_0^3} \sum_i n_i m_i (1 - d_i) \right]. \end{aligned} \quad (8)$$

Figure 3 shows how the different radii increase with increasing depletion. The grain has grown to 0.1  $\mu$  when the depletion of C<sup>+</sup> is about 1.5 (corresponding to  $2 \times 10^7$  years for an intercloud pressure of 1800 cm<sup>-3</sup> °K), and it reaches a radius of 0.16  $\mu$  when C<sup>+</sup> is depleted about 30 times (corresponding to  $\sim 10^8$  years), close to the largest possible radius of 0.17  $\mu$ . The “CH<sub>4</sub> grain” reaches its maximum radius faster than the H<sub>2</sub>O grain due to the larger depletion rate of C<sup>+</sup>.

The variation in the composition of the mantle during this phase is also shown in figure 3. CH<sub>4</sub> dominates the inner parts of the mantle, accounting for about 54 percent of the mantle material. Only if the grain reaches a radius of 0.15  $\mu$  or more will H<sub>2</sub>O be the most abundant constituent (averaged over the mantle), and for timescales less than a few  $10^8$  years (corresponding to  $T \lesssim 1000^\circ$  K), it never accounts for more than 50 percent of the mantle material. Thus, the “classical” dirty-ice composition of van de Hulst (1949), where H<sub>2</sub>O constituted about 60 percent of the grain material, is somewhat, but not greatly, modified. About 18 percent of the “classical” grain was H<sub>2</sub> molecules, of which there are none in this model. However, since H<sub>2</sub> molecules form in the strong adsorption sites, it is possible that some molecules could get trapped instead of immediately escaping upon recombining.

The equilibrium abundance of the molecular constituents were obtained by a numerical solution of the rate equations in § IV (tables 2 and 3). We employed a fourth-order Runge-Kutta integration method assuming constant temperature and hydrogen density. The time to reach equilibrium was in general  $\lesssim 10^4$  years, about  $10^3$  times less than the timescales for variations in temperature and density, justifying our assumption. The integration was stopped whenever the molecular abundances converged to within 0.5 percent.

It was assumed that the molecules would not affect the cooling rate, which is valid if the molecular abundance remains small compared with the atomic abundance. This condition is  $n_m \lesssim 10^{-6} n_{\text{H}}$  (Takayanagi and Nishimura 1960). In the preshock phase, the maximum molecular abundance is  $\sim 10^{-7}$  relative to H, so that the cooling will be dominated by atomic cooling as long as the depletion factor of O is  $d(\text{O}) \gtrsim 0.1$ .

Figure 4 shows the molecular abundances for a cloud of 200  $M_\odot$  as the cloud is depleted of cooling elements. We see that when the depletion is small, CO is the dominant molecule. However, as the grain grows larger, efficient formation of OH starts and this molecule is the most abundant when  $1/d(\text{C}^+) \approx 10$ . The increase in the abundance of OH and NH reflects, of course, the growth of the grain, since recombina-

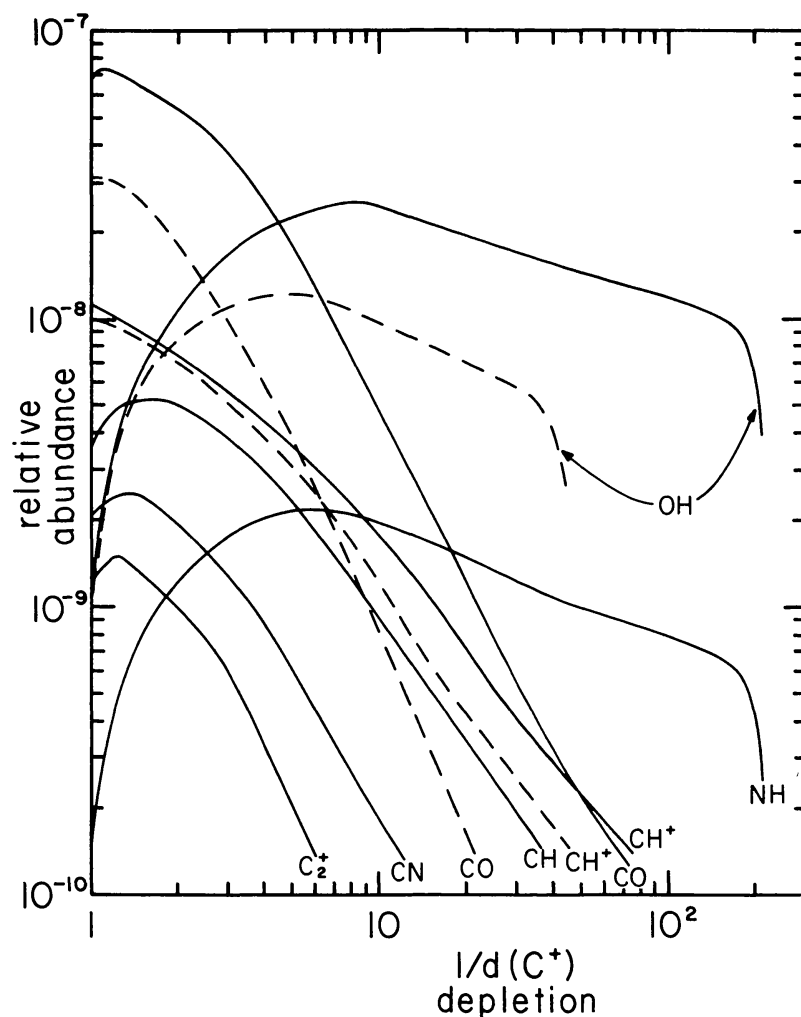


FIG. 4.—Molecular abundances in the gas phase relative to hydrogen as a function of the depletion of  $C^+$ . *Solid curves*, external pressure of  $1800 \text{ cm}^{-3} \text{ }^\circ\text{K}$ ; *dashed curves*, pressure of  $1000 \text{ cm}^{-3} \text{ }^\circ\text{K}$ . In both cases, the probability of a gas atom being retained in the grain as part of a molecule is  $\alpha = 0.5$ .

tion on the grain surface is the only formation process. The increasing grain radius also causes the extinction to increase, making this formation mechanism even more efficient. However, this effect is eventually dominated by the decrease in density (eq. [9]), and the maximum ultraviolet extinction is about 0.9 mag for depletion  $1/d(C^+) \approx 4$ . Since the albedo is 0.5, the attenuation of the radiation field is always small; the factor  $G$  (eq. [4]) never becomes smaller than 0.6 for this case. Since  $G$  is close to 1 and the extinction is only slowly varying with the cloud mass ( $A \propto M^{1/3}$ ; eq. [5]), figure 4 represents the molecular abundances for all the clouds considered ( $50\text{--}1000 M_\odot$ ) to within 50 percent.

With a higher grain extinction efficiency of  $Q(1000 \text{ \AA}) = 4$ , the molecular abundance increases only by less than 30 percent. The least affected is  $CH^+$ , since its primary destruction mechanism is not ultraviolet photodestruction but recombination with electrons. Thus the uncertainty in the optical characteristics of the grains will not change the results significantly for these types of clouds. The effect of a lower intercloud pressure of  $1000 \text{ cm}^{-3} \text{ }^\circ\text{K}$  is somewhat more important and is shown by the dashed curves in figure 4 for OH,  $CH^+$ , and CO. The maximum abundances for OH

and CO are lower by a factor of about 2, and CO will now dominate over OH for about twice as long (in time) as in the case of a pressure of  $1800 \text{ cm}^{-3} \text{ }^\circ \text{K}$ . This is mainly due to the density being lower (see fig. 2), decreasing the formation rates, and causing a slower buildup of the grain. The maximum abundance of  $\text{CH}^+$ , however, is about the same in the two cases, and a lower intercloud pressure gives a  $\text{CH}^+$  abundance that is actually larger by a factor of 5 for timescales  $> 5 \times 10^7$  years. This is due to the fact that the temperature changes slower with time for a smaller pressure, causing the temperature to remain fairly low and thus the radiative association rate of  $\text{C}^+ + \text{H}$  to remain high.

## VI. DISCUSSION

Observations at 21 cm of the intercloud medium (Rhadhakrishnan *et al.* 1972) and observed parameters for average clouds are consistent with the FGH model of the interstellar medium if  $\text{C}^+$  is depleted by a factor of  $\sim 0.1$  (Field, personal communication). From figure 1 we see that this corresponds to an average "age" of  $7 \times 10^7$  years. Although this may be comparable to the time since the last *complete* removal of cooling elements from the grains, it is much larger than the average cloud-cloud collision time of  $1 \times 10^7$  years, which is the time since the cloud was last in a cold and dense phase. Rather than use the "age" of a cloud, we will therefore use the depletion factors to indicate the physical state of a cloud. We define a "young cloud" and an "old cloud" as having a depletion factor for  $\text{C}^+$  that satisfies the inequalities  $0.1 < d(\text{C}^+) < 1$  and  $0.01 < d(\text{C}^+) < 0.1$ , respectively. These two types of clouds span the observed range of density and temperature for "normal" interstellar clouds ( $n_{\text{H}} = 10\text{--}100 \text{ cm}^{-3}$ ,  $T = 20^\circ\text{--}200^\circ \text{K}$ ).

Frisch (1972) has recently redetermined the column densities of interstellar CH,  $\text{CH}^+$ , and CN from the spectra of 30 stars as taken by Adams in 1949. Since most of these observations refer to a single absorption feature and to small amounts of interstellar extinction ( $A_v \lesssim 1$  mag) they should correspond well to the type of clouds that we have in mind. In table 4, we have listed the total range of column densities for these stars as well as a few representative cases. Theoretical values for the column densities based on the previous calculations are listed in table 4 for clouds with masses

TABLE 4  
OBSERVED\* AND CALCULATED† COLUMN DENSITIES FOR  $\text{CH}^+$ , CH, AND CN

Cloud	$N(\text{CH}^+)$ [ $10^{13} \text{ cm}^{-2}$ ]			$N(\text{CH})$ [ $10^{13} \text{ cm}^{-2}$ ]			$N(\text{CN})$ [ $10^{13} \text{ cm}^{-2}$ ]		
Total range for 30 stars....	0.4–2.7			0.8–4.0			0.4–8.0		
$\xi$ Per.....	$2.5 \pm 2.0$ – 1.2			$1.6 \pm 0.8$ – 0.6			...		
$\chi^2$ Ori.....	$1.1 \pm 1.3$ – 0.8			$1.7 \pm 1.2$ – 0.8			...		
$\chi$ Aur.....	$0.5 \pm 0.5$			$1.5 \pm 1.4$ – 0.9			...		
AE Aur.....	$4.1 \pm 3.0$ – 2.3			...			$0.4 \pm 0.2$		
$1000 M_\odot$ .....	2.5	1.7	0.28	1.5	1.5	0.21	0.74	0.67	0.04
$500 M_\odot$ .....	2.0	1.3	0.22	1.1	1.0	0.14	0.53	0.40	0.03
$200 M_\odot$ .....	1.5	1.0	0.16	0.74	0.67	0.08	0.36	0.25	0.02
$50 M_\odot$ .....	0.94	0.64	0.10	0.44	0.37	0.05	0.21	0.13	0.008

\* Observations from Frisch (1972).

† The three values entered for a given cloud correspond to the cloud having the depletion factors ( $\text{C}^+$ ) = 0.83, 0.51, and 0.11.



1000, 500, 200, and  $50 M_{\odot}$  in three different stages of depletion,  $d(C^+) = 0.83, 0.51$ , and  $0.11$ . We see that there is a general agreement with observations if  $d(C^+) \geq 0.5$ , i.e., if the observed clouds are fairly young clouds. However, CN is anomalously abundant in a few sources. For example, in 20 Aql no  $CH^+$  is observed and  $N(CN)/N(CH) = 2$ . This may be due to these clouds being much denser than considered here, possibly being in the compressed postshock phase. At high densities ( $n_H \geq 10^4 \text{ cm}^{-3}$ ), most of the carbon will be neutral (Werner 1970) and  $CH^+$  will not form efficiently. However, CH will form through radiative association and CN may be formed via  $CH + N \rightarrow CN + H$ .

Since the molecular abundances are sensitive to the state of depletion and this directly reflects the size of the grain, we may test our theory by comparing an "evolving" cloud with observations of both column densities and color excess. Bates and Spitzer (1951) pointed out that there seemed to be a correlation of the  $CH^+$  density with reddening. However, the recent observations by Frisch (1972) show that the detailed correlation as suggested by Bates and Spitzer is not substantiated. Instead, as shown in figure 5 (adapted from Frisch 1972), one finds clouds which have a large column density of  $CH^+$  and a small color excess as well as clouds with a large color excess and small  $CH^+$  column density, with most of the cases falling in between the extremes. There are no observations that show a large column density as well as a large color excess. In view of the results in § V, this has a ready explanation. The clouds with a large column density of  $CH^+$  and small color excess [e.g., cloud (1) in fig. 5] are young clouds which are relatively cold and dense and have small grains (very little depletion). As depletion increases, the  $CH^+$  density decreases and the extinction increases, causing a given cloud to move to the left and slightly upward in

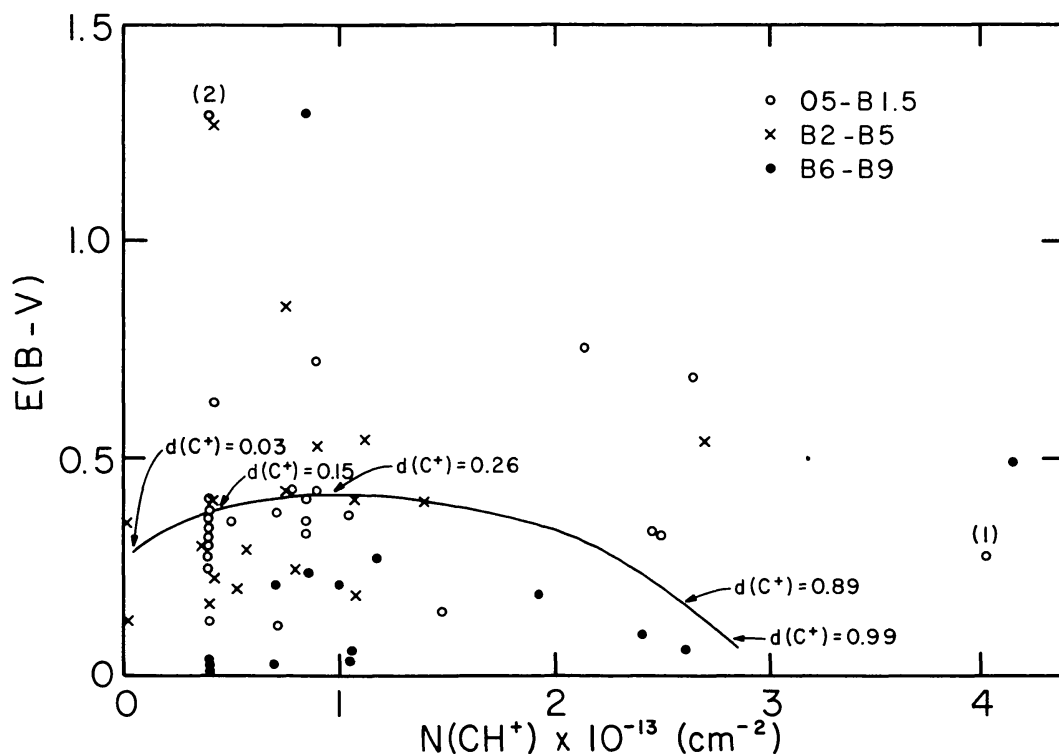


FIG. 5.—Points are observed values of color excess  $E(B - V)$  and  $CH^+$  column density as determined by Frisch (1972) for the three spectral groups indicated. Curve, predicted relationship for a cloud of  $1000 M_{\odot}$  as it goes through the various stages of depletion. Values for the depletion factor of  $C^+$  are indicated.

the diagram of  $E(B - V)$  versus  $N(\text{CH}^+)$ . The exact position of its track depends on the mass of the cloud, with a higher mass corresponding to larger color excess and column density. Eventually, the extinction reaches a maximum and starts to decrease with  $N(\text{CH}^+)$ . In figure 5 this evolution is plotted for a cloud of  $1000 M_\odot$ , assuming a ratio of total to selective extinction of 3 and a visual extinction efficiency of 1. If the initial radius of the grains were only slightly larger than  $0.05 \mu$ , e.g.,  $0.07 \mu$ , the curve in figure 5 would move upward by a factor of 2, corresponding roughly to the upper envelope of observed points, except for two points with very large color excess. We also note that the relative position of the two extreme clouds (1) and (2) in figure 5 corresponds almost exactly to what would be predicted on the basis of figure 3 (for the color excess) and figure 4 (for the column density of  $\text{CH}^+$ ) if we assign an "age" of  $10^7$  years [ $1/d(\text{C}^+) = 1.1$ ] to cloud (1) and an age of  $10^8$  years [ $1/d(\text{C}^+) = 33$ ] to cloud (2), assuming that they have about the same column density of neutral hydrogen. (The latter cloud is then more massive, since it has a much lower density.) We conclude that the effect of depletion on the molecular abundances and extinction may account for the distribution of the observed points in figure 5. Also, the predicted column densities of  $\text{CH}^+$ ,  $\text{CH}$ , and  $\text{CN}$  based on the rates given by Klemperer (1971) are in agreement with observations. However, observations of temperatures, neutral hydrogen densities, and depletion factors are most important tests; these await further determination.

Some of the observed properties of a "hydroxyl cloud" of the sort we are concerned with have recently been given by Davies and Matthews (1972) and are listed in table 5. We have also listed the parameters of a cloud of  $500 M_\odot$  having a depletion factor  $d(\text{C}^+) = 0.1$ . We see that the calculated OH abundance is smaller than the observed value by about a factor of 3, but falls within the range as given by Goss (1967). Given all the uncertain parameters, we feel that this is a reasonable agreement. Davies and Matthews find that the abundance of molecules increases with the abundance of neutral hydrogen for this type of cloud. From figures 2 and 4, we see that this is to be expected for clouds with  $T \gtrsim 50^\circ \text{K}$ ,  $n_{\text{H}} \lesssim 30 \text{ cm}^{-3}$ , since these are clouds for which all the molecules considered fall in abundance due to the expansion of the cloud. For cooler and denser clouds, however, we would expect an anticorrelation in the case of OH (see the discussion below of  $\zeta \text{ Oph}$ ).

Recently, a preassociation mechanism has been proposed for the formation of OH (Julienne *et al.* 1971). For the clouds considered here, their rate of  $1.3 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$  is too small to account for the observations by at least two orders of magnitude. Only if the grain formation mechanism is prohibited for some reason (e.g., a grain temperature that is too high) will this be an important formation rate for OH. We conclude that the formation of OH on grain surfaces with subsequent ejection into the gas phase explains the observations of OH in "typical" clouds within a factor of 3. In

TABLE 5  
PARAMETERS OF A HYDROXYL CLOUD

Parameter	Observations*	Calculations†
Column density $N_{\text{H}}$ ( $\text{cm}^{-2}$ )	$1.1 \times 10^{21}$	$1.1 \times 10^{21}$
Temperature $T_{\text{H}}$ ( $^\circ \text{K}$ )	50–100	52
Density $n_{\text{H}}$ ( $\text{cm}^{-3}$ )	36	35
Extinction $A_v$ (mag)	0.2–0.4	0.4
OH abundance OH/H	$\sim 10^{-7}$	$3 \times 10^{-8}$
$\text{H}_2\text{CO}$ abundance $\text{H}_2\text{CO}/\text{H}$	$\sim 2 \times 10^{-9}$	...

\* Observations as given by Davies and Matthews (1972).

† Calculations for a cloud of  $500 M_\odot$  with depletion  $d(\text{C}^+) = 0.1$ .

contrast to the type of clouds where  $\text{CH}^+$ ,  $\text{CH}$ , and  $\text{CN}$  form efficiently, i.e., in young clouds,  $\text{OH}$  should be most abundant in the older, i.e., more depleted, clouds. This may explain why  $\text{OH}$  has not been seen in clouds where  $\text{CH}^+$  and  $\text{CH}$  have been seen optically.

From table 5 we see that the observed abundance of formaldehyde is  $\text{H}_2\text{CO}/\text{H} \sim 2 \times 10^{-9}$ . If we make the optimistic assumptions that every  $\text{CO}$  molecule can form  $\text{H}_2\text{CO}$  efficiently (combining with  $2\text{H}$  or  $\text{H}_2$ ) on the grain surface and that  $\text{H}_2\text{CO}$  is destroyed only through photodissociation with a rate of  $7 \times 10^{-10} \text{ G s}^{-1}$ , then we have for equilibrium conditions

$$\frac{\text{H}_2\text{CO}}{\text{H}} = 10^{-8} n_{\text{H}} \left( \frac{T}{100} \right)^{1/2} \frac{a^2}{G} \left( \frac{\text{CO}}{\text{H}} \right), \quad (9)$$

where  $a$  is the grain radius in units of  $10^{-5} \text{ cm}$ ,  $G$  is the attenuation of the radiation field, and the other symbols have their usual meanings. Since the  $\text{CO}$  abundance for a cloud as specified by the temperature and density in table 5 is  $\sim 10^{-8}$  relative to  $\text{H}$  (fig. 5), and  $G \sim 0.8$ , we see that a grain formation mechanism for  $\text{H}_2\text{CO}$  fails by many orders of magnitude in this case. Only if the  $\text{CO}$  abundance is as large as the atomic oxygen abundance—recent observations (Penzias, Jefferts, and Wilson 1971) indicate that this may be the case—or the extinction is several magnitudes could  $\text{H}_2\text{CO}$  form efficiently on the grains.

Due to the lack of uniform conditions in interstellar clouds, it is clear that detailed observations of both atomic and molecular abundances in single clouds are needed to effectively test the theoretical assumptions. The only interstellar cloud which has been studied in such detail is the cloud in front of  $\zeta \text{ Oph}$  (Herbig 1968). In table 6 we have listed the observations of column densities by Herbig, the calculations by Solomon and Klemperer (Klemperer 1971), as well as two sets of column densities for an interstellar cloud of  $500 M_{\odot}$  in two different states of depletion.

We see that in order to be consistent with the upper limits on  $\text{OH}$  (and  $\text{NH}$ ), this theory requires that the cloud be a “young” cloud, with depletion  $1/d(\text{C}^+) \approx 1.1$ , i.e., it is cold ( $T \sim 20^\circ \text{ K}$ ) and fairly dense ( $n_{\text{H}} \approx 90 \text{ cm}^{-3}$ ). Since the density is higher than what Solomon and Klemperer considered, the agreement with observation of  $\text{CH}$  and  $\text{CH}^+$  is actually somewhat improved. However, the extinction in this phase is

TABLE 6  
COLUMN DENSITIES OF MOLECULES IN  $\zeta \text{ OPH}$

Molecule	Observed [ $\text{cm}^{-2}$ ]	Calculations* [ $\text{cm}^{-2}$ ]	Calculations† [ $\text{cm}^{-2}$ ]	Calculations‡ [ $\text{cm}^{-2}$ ]
$\text{CH}$ .....	$4.3 \times 10^{13}\S$	$9.0 \times 10^{12}$	$1.0 \times 10^{13}$	$9.0 \times 10^{12}$
$\text{CH}^+$ .....	$2.6 \times 10^{13}\S$	$9.1 \times 10^{12}$	$2.1 \times 10^{13}$	$1.0 \times 10^{13}$
$\text{CN}$ .....	$8.3 \times 10^{12}\S$	$7.8 \times 10^{12}$	$5.5 \times 10^{12}$	$3.3 \times 10^{12}$
$\text{OH}$ .....	$< 9.0 \times 10^{12}\S$	0	$6.0 \times 10^{12}$	$2.7 \times 10^{13}$
$\text{NH}$ .....	$< 7.0 \times 10^{13}\S$	0	$7.5 \times 10^{11}$	$3.0 \times 10^{12}$
$\text{CO}$ .....	$\lesssim 7.6 \times 10^{15}\parallel$	$1.1 \times 10^{14}$	$1.7 \times 10^{14}$	$9.4 \times 10^{13}$

\* From Klemperer (1971), who assumed  $T = 20^\circ \text{ K}$ ,  $n_{\text{H}} = 50 \text{ cm}^{-3}$ ,  $N_{\text{H}} = 1.5 \times 10^{21} \text{ cm}^{-2}$ , and  $A_v = 0.5 \text{ mag}$  (visual extinction to the center of the cloud).

† For a cloud of  $500 M_{\odot}$  with  $d(\text{C}^+) = 0.89$ ,  $T = 20.1^\circ \text{ K}$ ,  $n_{\text{H}} = 90 \text{ cm}^{-3}$ ,  $N_{\text{H}} = 2 \times 10^{21} \text{ cm}^{-2}$ , and  $A_v = 0.2 \text{ mag}$ .

‡ As in † with  $d(\text{C}^+) = 0.39$ ,  $T = 26.5^\circ \text{ K}$ ,  $n_{\text{H}} = 68 \text{ cm}^{-3}$ ,  $N_{\text{H}} = 1.7 \times 10^{21} \text{ cm}^{-2}$ , and  $A_v = 0.5 \text{ mag}$ .

§ From Klemperer (1971), based on Herbig's (1968) observations.

|| From Smith and Stecher (1971).

smaller than the observed value by a factor of 2.5. When the extinction becomes larger, the abundance of OH (and NH) also becomes larger, due mostly to a higher formation rate because of the larger grains. As is shown in the last column of table 6, OH is more abundant than  $\text{CH}^+$  when the extinction corresponds to the observed value, violating the upper limit set by Herbig by about a factor of 3.4. Such a discrepancy may not be considered a disagreement in view of the inherent uncertainties in the rates, especially in the case of OH, where we may have underestimated the photo-destruction rate (§ IV). In addition, uncertainties about the initial grain radius, the escape probability of a newly formed OH molecule, as well as the temperature of the grains in the  $\zeta$  Oph cloud could all remove this discrepancy between extinction and the limiting OH column density.

It is clear from table 6 that the recent observation of CO in  $\zeta$  Oph (Smith and Stecher 1971) shows CO to be more abundant than predicted by at least a factor of 10–50. Although it is likely that the CO photodissociation rate has been overestimated (Klemperer, personal information), it may be difficult to account for such a large difference. We have noted before that the predicted CO abundance is much too small to account for the observed abundance of  $\text{H}_2\text{CO}$  through formation on grains for the type of clouds considered here. Observations by Penzias *et al.* (1971) in a number of well-known objects gave column densities as large as  $\sim 10^{19} \text{ cm}^{-2}$ . Although theory shows CO to be the most abundant diatomic molecule, more efficient formation mechanisms seem required to explain the observations in sources with small ultraviolet extinction. We conclude, however, that except for CO, the molecules observed and the molecules searched for in the cloud of  $\zeta$  Oph are consistent with the cloud being a young cloud which is still fairly cold and dense, with small interstellar grains and thus low formation rates of OH and NH.

We have noted that infrared absorption observations (Knacke *et al.* 1969) place a rather strict upper limit on the average amount of  $\text{H}_2\text{O}$  in interstellar grains. However, these observations have all been done on heavily reddened stars, assuming that all the reddening is due to interstellar dust. It may be that part of the reddening is due to circumstellar material (Gaustad 1971), and since the temperature of such grains is likely to be higher than for the average interstellar grain, we would not expect ice mantles to form on circumstellar grains. Unless contributions from circumstellar reddening can be definitely ruled out, the results are not conclusive for the composition of interstellar dust. On the other hand, the existence of the peak in the extinction curve at  $2200 \text{ \AA}$ , if due to graphite, also sets a rather strict limit on the size of any mantle (Code 1971). If mantles form under average interstellar conditions in the way we have outlined above, it seems probable that efficient mantle removal processes must exist in order to satisfy the observations. One such process is sputtering of the mantles by the hot atoms in shock waves during cloud-cloud collisions. In a subsequent paper we will investigate this process in the postshock evolution of interstellar clouds.

In an investigation simultaneous with our own, Watson and Salpeter (1972*a*, 1972*b*) have shown that photoejection by ultraviolet starlight of physically adsorbed molecules could be an efficient process for keeping the grain surface "clean." Also, ejection probabilities as large as unity have been found in a laboratory study of photodesorption from a silicate surface (Greenberg 1972). A photoejection probability larger than about 0.01 will effectively hinder mantle growth and limit the possibilities of complex molecule formation through surface reactions for relatively unshielded clouds. However, photoejection may be efficient only for molecules that are different from the surface particles, and photoejection of  $\text{H}_2\text{O}$  from an ice crystal is inhibited (Watson and Salpeter 1972*a*). In terms of the model of grain growth outlined above, it is then a question of whether or not the first monolayer will form on the core. Since the laboratory results are still preliminary, we conclude that it is within the



uncertainties that mantle growth will occur but that revisions may be necessary if the ejection probability is indeed of the order of unity.

Recently, Watson (1972) has found that grains in unshielded H I regions may acquire a net positive charge because of photoelectric emission. This would severely limit any depletion of the positively charged trace elements onto the grain cores. On the other hand, depletion of the neutral species O and N could make the grains more icelike, and such grains are expected to become negatively charged (Watson 1972). We also note that recent observations (Chaffee *et al.* 1972; White 1973) indicate that depletion of charged trace elements does occur in interstellar clouds.

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